

✓  
**THE EFFECT OF CASTING CONDITIONS AND CASTING SOLUTION  
COMPOSITION ON CELLULOSE ACETATE  
DESALINATION MEMBRANES**

A Thesis Submitted  
In Partial Fulfilment of the Requirements  
for the Degree of  
MASTER OF TECHNOLOGY

By  
NIRMAL KUMAR AGARWAL

CENTRAL LIBRARY.  
INDIAN INSTITUTE OF TECHNOLOGY, KANPUR

to the  
DEPARTMENT OF CHEMICAL ENGINEERING  
INDIAN INSTITUTE OF TECHNOLOGY KANPUR  
MAY 1974

V  
JUNE '76

I.I.T. KANPUR  
CENTRAL LIBRARY  
Acc. No. A 29865

✓ CHE-1974-M-AGA-EFF

6 AUG 1974

Thesis  
668.44  
Ag15

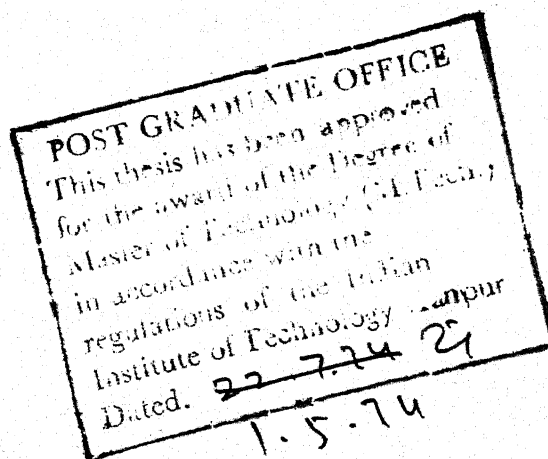
CERTIFICATE

This is to certify that the present work has been done under my supervision and has not been submitted elsewhere for a degree.

Date: 29th April 1974

*Kamalg Sirkar*

Dr. K.K. Sirkar  
Assistant Professor  
Department of Chemical Engg.  
Indian Institute of Technology  
Kanpur-208016, India



ACKNOWLEDGEMENTS

I express my deep sense of gratitude to Dr. K.K. Sirkar for suggesting the problem and providing his valuable guidance and constant encouragement throughout this work. That apart, his readiness to lend a helping hand in the experimental work has been very instructive and inspiring.

Thanks are due to Eastman Kodak Company, U.S.A. for the timely supply of their 3 grades of cellulose acetate free of cost which was very essential for the work.

The encouragement during this work from friends specially from Mr. Dhirendra Kumar, Mr. C.P. Agrawal and Mr. R.K. Gupta is very appreciative.

I am thankful to the staff of the Chemical Engineering Workshop for their constant help and co-operation.

The help of Mr. B.S. Pandey is highly appreciated for typing the manuscript.

Nirmal

### ABSTRACT

Cellulose acetate desalination membranes have been cast using higher concentrations of cellulose acetate in Manjikian type casting formulation. The air exposure period has been reduced to very low values of 0.1-0.2 seconds. Tests have been made with a feed solution containing 0.5% by weight NaCl at 600 psig to simulate typical brackish water conversion conditions. These membranes are capable of giving a flux of upto 28 gfd with 98% salt rejection which is excellent by any standard. Another membrane has yielded at a lower temperature of annealing a flux of 58.5 gfd and 91.8% salt rejection which is better than any known membrane. Another feature of membranes having 31.5% CA in the casting solution is that high salt rejection is achieved at an annealing temperature as low as 74°C thus pointing towards possibilities of having a desalination membrane that does not need any annealing.

\*\*\*\*

CONTENTS

CHAPTER			PAGE
I	INTRODUCTION	...	1
II	MEMBRANE PERFORMANCE CRITERIA	...	4
III	PREVIOUS WORK ON FLUX IMPROVEMENT	...	6
IV	MECHANISM OF MEMBRANE FORMATION	...	10
	(a) Influence of air exposure period on membrane structure	...	10
	(b) Evaporation of acetone and formation of two thick layers	...	10
V	PRESENT WORK	...	12
VI	EXPERIMENTAL DETAILS	...	16
	(a) Preparation of casting solution		16
	(b) Casting of cellulose acetate membranes		16
	(c) High pressure membrane testing loop		18
	(d) Testing of membranes at high pressure		23
VII	RESULTS AND DISCUSSION	...	25
	REFERENCES	...	32
	APPENDIX	...	33

...

...

LIST OF FIGURES

FIGURE		PAGE
1	Membrane Performance as a Function of Evaporation Time     ...     ...	8
2	Phase Diagram of the System Cellulose Acetate -Formamide-Acetone     ...	13
3	Schematic Diagram of Vertical Membrane Casting Set-up     ...     ...	19
4	High Pressure Membrane Testing Loop	20
5	Reverse Osmosis Cell     ...     ...	22

...

LIST OF TABLES

TABLE		
1	Performance of Membranes Cast on Horizontal Table     ...     ...	26
2	Performance of Membranes Cast on Vertical Table     ...     ...	27

...

## CHAPTER I

### INTRODUCTION

The increasing demand for fresh water from saline water has, in the last twenty years, stimulated extensive investigations into newer and more economic processes for desalination of sea and brackish water. Reverse Osmosis or hyperfiltration has been in the forefront of these newer processes. The earliest investigations to find a suitable membrane material for reverse osmosis were carried out by Reid and Breton (1) in 1956. They found out that cellulose acetate was far superior to other membrane materials with respect to its semipermeability to sea-water salts and its water flux. However, this value of water flux was still very low for practical purposes. The commercial prospects for reverse osmosis was brightened considerably in 1960, when Loeb and Sourirajan (2) fabricated a high flux semi-permeable membrane from a solution of cellulose acetate having a composition of 22% cellulose acetate (CA), 66.7% acetone, 1.1% magnesium perchlorate and 10% water. This solution at a temperature around  $-5^{\circ}\text{C}$  was cast uniformly on a cold glass plate at  $-10^{\circ}\text{C}$  with a doctor's blade and exposed to air for about 3 minutes, after which it was gelled into a thin film by immersion in ice water for an hour. Desalination properties were obtained by shrinking



the membrane for 5 minutes in hot water (65 to 85°C). Extensive morphological studies of this membrane indicated an asymmetric structure consisting of a thin  $0.25\mu$  dense layer at the top formed by the loss of acetone in air supported on a porous substructure when the total membrane thickness was  $100\mu$ . The surface layer of a membrane before annealing showed no evidence of pores bigger than  $100\text{ \AA}$  whereas the porous substructure underneath the surface layer had pores of size 1000 to  $4000\text{ \AA}$ . After heat treatment, the pores in the top layer are of size 4 - 9  $\text{ \AA}$ .

Considerable simplicity was achieved when Manjikian, Loeb and McCutchan (3) fabricated in 1965 a cellulose acetate membrane from a 25% CA - 30% formamide - 45% acetone solution by casting it at room temperature with a 30 second evaporation time. This membrane's flux and salt rejection characteristics were comparable to those of Loeb-Sourirajan membrane. It is believed that cellulose acetate membranes commonly used in the industry in U.S.A. and for research purposes are obtained by this latter method. For example, Eastman Kodak membranes are supposed to be of this type. These cellulose acetate membranes have, however, certain limitations. For example, they should not be used outside a pH range of about 4 - 8; they must be used at temperatures lower than 80°C; there are possibilities of bacterial growth and degradation in adverse environments. These shortcomings are genuine as

cellulose acetate has been found to be an extremely versatile semi-permeable membrane for an extremely wide variety of separation processes for removing small solutes from primarily aqueous solutions. This has encouraged research on membrane materials other than cellulose acetate (4). Yet cellulose acetate continues to be the dominant membrane in the field of small solute separations.

This dominance has prompted extensive research towards improving upon existing cellulose acetate membranes. Efforts have been made

- (a) to improve the compaction resistance of the membrane
- (b) to increase the water flux through the membrane at a given salt rejection for a given operating pressure, and
- (c) to increase the salt rejection characteristics for the fabrication of membranes suitable for desalination of sea water by one pass at 1500 psi

The present work is directed towards the following two objectives:

1. to fabricate CA desalination membranes which are comparable with the best available.
2. to increase the water flux as in (b) mentioned above and to understand the mechanism for such increases in water flux if possible.

## CHAPTER II

### MEMBRANE PERFORMANCE CRITERIA

The performance of a membrane for desalination of brackish water is measured in terms of two quantities, namely, (a) per cent salt rejection and (b) the flux of permeate through the membrane when tests are conducted with brine feed at 600 psig flowing over the membrane at 25°C. The feed is an aqueous solution of 0.5% NaCl by weight. The percent salt rejection is defined as

$$\% \text{Salt rejection} = R = \left( 1 - \frac{\text{NaCl concentration in permeate}}{\text{NaCl concentration in feed}} \right) \times 100 \quad (1)$$

Permeate flux  $F$  is defined as the amount of permeate per unit area of membrane surface per unit time. The commonly used unit for flux in literature is gallons/(ft<sup>2</sup>)(day) abbreviated as gfd (U.S. gallons). Corresponding unit in metric system is litres/m<sup>2</sup>/day and the conversion factor is

$$1 \text{ gfd} = 0.0414 \text{ litres/m}^2/\text{day} \quad (2)$$

Here we will be reporting the flux in gfd. Some workers prefer to use a salt reduction factor,  $S$ , instead of  $R$  to denote the extent of semipermeability of the membrane to salt. This factor is defined in the following manner:

$$\text{Salt Reduction Factor (S)} = \frac{\text{NaCl concentration in feed}}{\text{NaCl concentration in permeate}} \quad (3)$$

It is well known that the water flux through the membrane increases with increase in operating temperature (see page 176 of Ref.(5)). Further Sourirajan (5) has observed that the product of the permeate flux and the viscosity of the feed is a constant. Therefore the relationship between flux measured at  $t^{\circ}\text{C}$  and that at  $25^{\circ}\text{C}$  is

$$(F_{25^{\circ}\text{C}}) \times (\mu_{25^{\circ}\text{C}}) = (F_{t^{\circ}\text{C}}) \times (\mu_{t^{\circ}\text{C}}) \quad (4)$$

$$\text{or } F_{25^{\circ}\text{C}} = (F_{t^{\circ}\text{C}}) \times \frac{(\mu_{t^{\circ}\text{C}})}{(\mu_{25^{\circ}\text{C}})} \quad (5)$$

where  $\mu$  is the viscosity of the permeate.

## CHAPTER III

### PREVIOUS WORK ON FLUX IMPROVEMENT

It is known that the intrinsic permeabilities of water and salt decrease with increasing acetyl content. But the fact that permeability of the salt decreases more rapidly than that of water (1), has encouraged researchers to make blend membranes of cellulose diacetate and cellulose triacetate (CTA) so that membranes with higher salt rejection can be obtained. King et.al (4) prepared 10 mils thick cellulose acetate blend membranes on a moving aluminized Mylar belt from a casting formulation of 55 gm. dioxane, 35 gm. acetone, 9 gm. methanol, 3 gm. maleic acid, 10 gm. of cellulose diacetate (E - 398-3) and 10 gm of cellulose triacetate (A-432 - 130B). The film was gelated in 1°C water after an evaporation time of 60 - 90 seconds. They concluded that these membranes exhibit salt rejection properties superior to conventional cellulose diacetate membranes and are capable of producing potable water from seawater in a single pass with initial fluxes of 11 to 13 gfd and salt rejections of 99.3 to 99.6 at a pressure of 1500 psi.

It has also been thought that if the total amount of acetone lost by evaporation from the top of the membrane during the air drying period can be reduced, the thickness of the dense salt-rejecting skin in the asymmetric membrane

will be smaller and other things remaining same, the water flux through the membrane would be increased. McCutchan (6), therefore, determined the performance of membranes cast from a Manjikian type casting solution having a composition of 25:30:45 by weight of CA (E-398-10), formamide, acetone with variable evaporation time. In Figure 1, his results are plotted as a function of evaporation time (going to values as low as 0.015 second). Permeabilities of salt and water decrease with increasing evaporation time. Water flux drops by 50% between 0.1 second and 30 seconds while it decreases very rapidly to 6 gfd for 60 seconds evaporation time. The salt reduction factor S increases from 3 to about 21 over the same range of evaporation times with a large increase occurring between 1.0 and 5.0 seconds. One may conclude from McCutchan's work that going to very small evaporation times may improve the flux but the salt rejection will be drastically reduced so that the membrane is not very useful.

Asymmetric cellulose acetate desalination membranes of Loeb-Sourirajan type or Manjikian type are porous phase-inversion membranes. In such membranes, the performance characteristics are primarily determined by the primary gel structure obtained by drying and gelation. This gel structure is affected by the casting solution composition, casting and gelation conditions. Fahey and Grethlein (7) varied the casting solution composition and the evaporation time of a

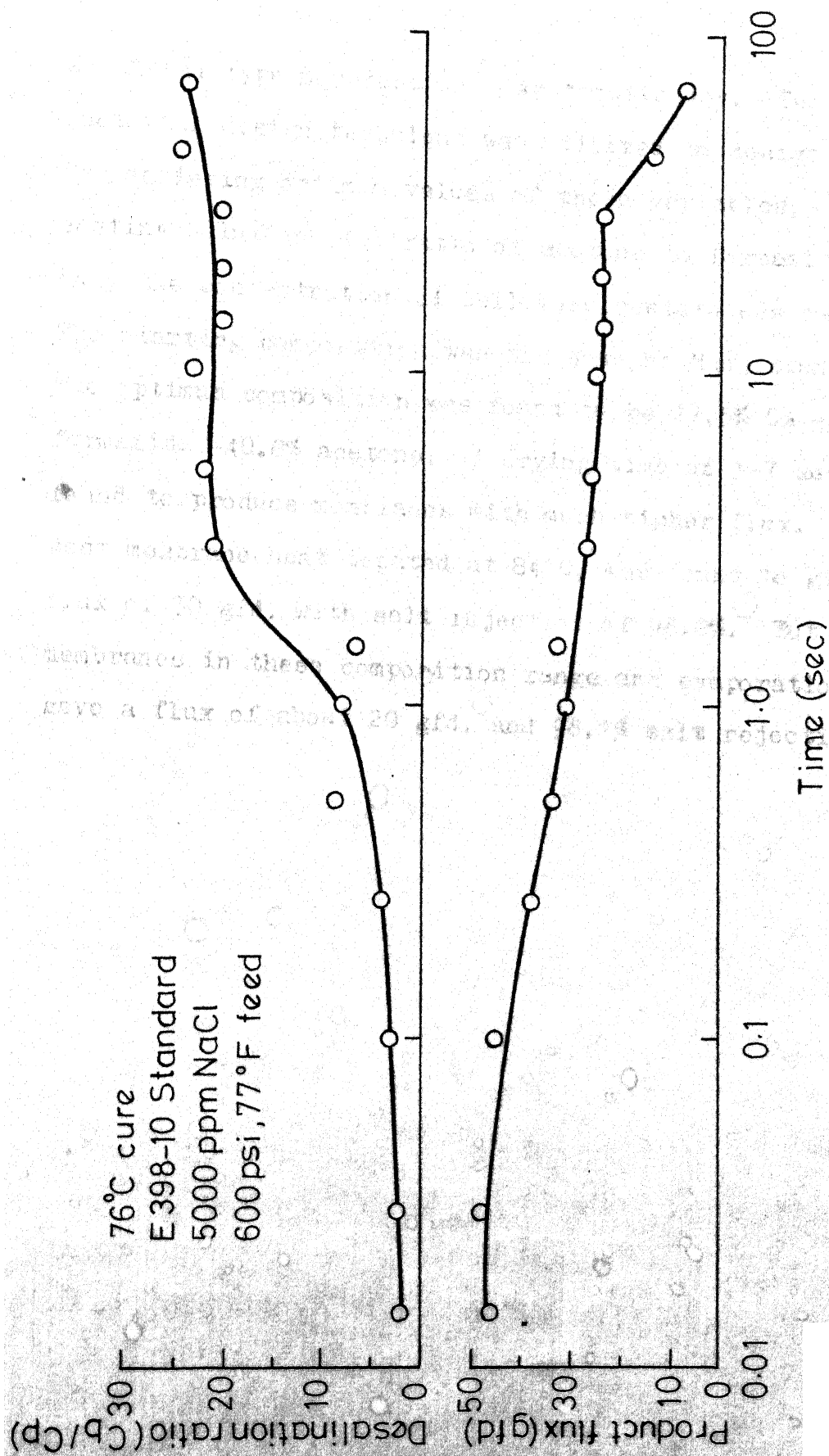


Fig. 1 - Membrane performance as a function of evaporation time.

Manjikian type membrane in a systematic way. A two level factorial design technique was utilized to design experiments for achieving optimum values of these variables. In the casting solution, the ratio of acetone to formamide was fixed; only the concentration of cellulose acetate was varied. The starting composition was the same as Manjikian's composition. The optimum composition was found to be 27.5% CA - 31.7% formamide - 40.8% acetone. A drying time of 1-7 seconds was found to produce membranes with much higher flux. Their best membrane, heat treated at 84°C, was found to give a flux of 30 gfd. with salt rejection of 98.0%. But the average membranes in these composition ranges and evaporation times gave a flux of about 20 gfd. and 98.1% salt rejection.



## CHAPTER IV

### MECHANISM OF MEMBRANE FORMATION

#### (a) Influence of Air Exposure Period on Membrane Structure:

On the basis of scanning electron micrographs of cross-section of membranes cast from cellulose acetate solution of Manjkikian's composition with different evaporation times prior to their gelation in the ice-cold water, Frommer and Lancet (4) suggested the existence of two distinguishable layers, with the upper one being much denser in the partially air-dried membrane. The thickness of the dense layer increases from 10 percent of the thickness for the membrane obtained by 5-10 second evaporation time to practically the total thickness for the membrane having 5 minutes evaporation time.

Further it was observed by Frommer and Lancet (4) that the rate of evaporation of acetone was very high immediately after film casting with very little change occurring after 5 minutes of air exposure. This prompted them to suggest the dense layer is formed as a result of acetone evaporation.

#### (b) Evaporation of Acetone and Formation of Two Thick Layers:

The composition of Manjkikian's solution is such that about 20% loss of acetone content from the top layer induces the sol-gel transition within the upper layer of the cast film. Since the evaporation of acetone is very fast, there

will be a layer of solidified gel on top of the still fluid casting solution in the film in a short time. The thickness of this layer increases rapidly with increase in evaporation time as the rate of acetone evaporation is very high in the initially period. The borderline between the upper solidified gel and the lower fluid casting solution is quite sharp and the immersion of such a film in the precipitating bath of ice cold water will yield an asymmetric membrane. The upper solidified gel layer becomes the dense skin and the lower fluid casting solution becomes the thick porous substructure of the membrane. This has been confirmed by electron microscopic studies of the cross-section of these membranes (4).

## CHAPTER V

### PRESENT WORK

Our initial efforts have been directed towards casting membranes with the improved composition of casting solution and low evaporation times of 1-7 seconds recommended by Fahey et al (7). This was necessary for establishing reliability of our experiments. Fahey et.al (7) did not experiment with evaporation times lower than 1 second. Since it is clear from the work of Frommer and Lancet (4) that the skin becomes thicker as the evaporation time increases, the permeate flux should decrease with increasing evaporation time, as exemplified by the flux of 1-7 second membranes by Fahey et al (7). It is obvious that the performance of membranes having evaporation times of less than 1 second should be investigated. McCutchan and Johnson (6) have, however, tested membranes cast from Manjikian composition with evaporation times as low as 0.015 seconds and have found high flux but very poor salt rejection at very low evaporation times. It is felt that the casting solution composition has to be drastically changed to improve the salt rejection at these low evaporation times. At these low evaporation times, the amount of acetone evaporated would be very small and the upper layer of a Manjikian membrane may not undergo a sol-gel transition. It is necessary, therefore, to have a casting composition which is very close to the

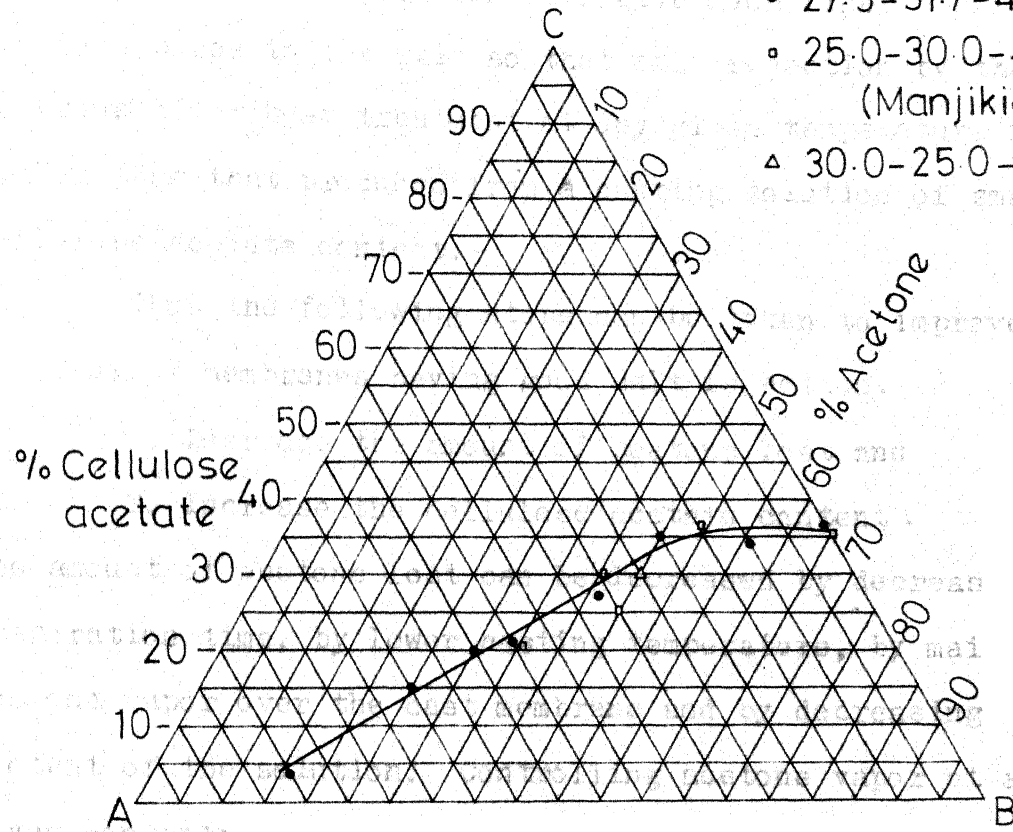


Fig. 2 - Phase diagram of the system cellulose acetate  
formamide - acetone (25°C)  
used cellulose acetate content.

saturation line in Figure 2. Further, higher polymer concentration will provide numerous small droplets in the remaining liquid matrix (see Kesting (8) page 121-122).

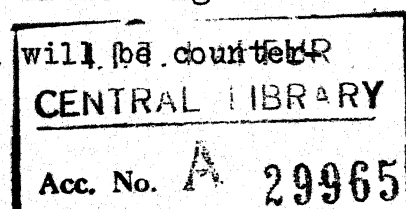
This membrane after gelation will give much finer and more numerous pores in the skin so that salt rejection by the membrane after heat treatment at any given temperature ~~is~~ will be higher than that produced from a casting solution of smaller cellulose acetate content.

Thus the following steps can be taken to improve the flux of membranes having good salt rejection:

1. Decrease the amount of acetone lost and
2. Increase the cellulose acetate content.

The amount of acetone lost can be decreased by decreasing evaporation time, by lower casting temperature, by maintaining acetone vapor over the cast membrane and by decreasing acetone content of the solution. Controlling acetone vapor at a given concentration level over the film was found to be quite difficult. Acetone content of the solution can be decreased only upto the solubility curve. We have therefore operated under conditions of decreased evaporation time, lower casting temperature and increased cellulose acetate content. The results section reports some of the preliminary results that we have obtained.

It must be pointed out however that increasing cellulose acetate content beyond some level will be counter



productive since the membrane skin and the porous sub-structure may become too dense and the flux may be reduced considerably. It may be more useful to incorporate small amounts of salts like  $\text{ZnCl}_2$ ,  $\text{ZnBr}_2$ ,  $\text{ZnI}_2$  which may act as (a) nucleating agents producing larger number of finer pores or as (b) a swelling agents increasing the permeability of the membrane.

## CHAPTER VI

### EXPERIMENTAL DETAILS

#### (a) Preparation of Casting Solution:

The casting solution was prepared from E-398-3 grade cellulose acetate (obtained from Eastman-Kodak Chemicals, U.S.A.), analytical reagent grade formamide (E. Merck, W. Germany) and analytical reagent grade acetone (BDH). The cellulose acetate E-398-3 was used in the powder form as obtained from the manufacturer without any treatment. The casting solutions were prepared in ~~the~~ batches of 150 gms in a conical flask fitted with standard glass joint and stopper. All the membranes were cast in an atmosphere at ambient temperature. The membranes were stored in distilled water at room temperature. To avoid undesirable bacterial growth on the membrane two drops of 40% W/V formaldehyde solution were added in 1 litre of the water in which membranes were kept.

#### (b) Casting of Cellulose Acetate Membranes:

In our initial experiments, the membranes were cast on a glass plate which was moved straight along its length on a horizontal supporting brass table with guides. The casting solution was spread across the width of the glass plate near a doctor's blade set parallel to the glass plate width. The gap between the doctor's blade and the glass plate

was fixed at a very small value, say, 0.006" by means of feeler gauges so that the membrane as cast would have the same thickness. The wiped film was allowed to dry in air for a fixed time after which it was kept immersed in ice-cold water bath at 1-4°C for gelation for 1 hour. The membrane floated off the plate after sometime after which the skin side of the membrane was marked with an indicator. The minimum evaporation time that could be achieved in this manner was never less than 2 seconds.

To decrease the evaporation time to values lower than 2 seconds, the glass plate with the cast membrane on it was pulled along the brass table on which ice cold water was flowing at a short distance from the doctor's blade. Acetone was lost from the cast membrane in the small air gap between the blade and the flowing ice-cold water. One could achieve evaporation times as small as 0.1 seconds in this manner. But water flowing over the membrane had some waves always which are likely to create wavemarks (see page 134 in (4)) on the membrane skin. These wavemarks usually crack under high pressure while testing. As a result they provide channels through which salt leaks and the salt rejection is substantially reduced.

After a few experiments in most of which membranes had poor salt rejection this set-up was abandoned. The arrangement, finally adopted for small evaporation times, consists of a vertical brass plate with guides along which glass plates



can slide down smoothly. The doctor's blade was kept almost horizontally at a small distance (say, 0.008") away from the glass plate. The casting solution was poured between the glass plate and the doctor's blade. The plate was pushed down with hand at as uniform a speed as possible into an ice cold water bath whose level could be brought up to almost the blade. Thus the thickness of the airgap could be reduced or increased to provide for the desired evaporation time. The speed of the glass plate can also be varied to control the evaporation time. In this arrangement, the membrane enters stagnant water; so the possibilities of wave marks on the skin is minimal especially at low speeds. The results with vastly improved salt rejection testify to this. This arrangement is shown schematically in Figure 3. The speed of the glass plate was varied between 5 ft/min to 8 ft/min. and was determined by means of a stopwatch. For an airgap of 1/8 inch, 5 ft/min. speed would give an evaporation time of 1/8 seconds.

(c) High Pressure Membrane Testing Loop:

The high pressure membrane testing setup is drawn schematically in Figure 4. This consists of the feed tank, high pressure reciprocating pump, surge tank, reverse osmosis cell, pressure indicating gauge, purge valve and a back pressure regulator. All parts coming in contact with the

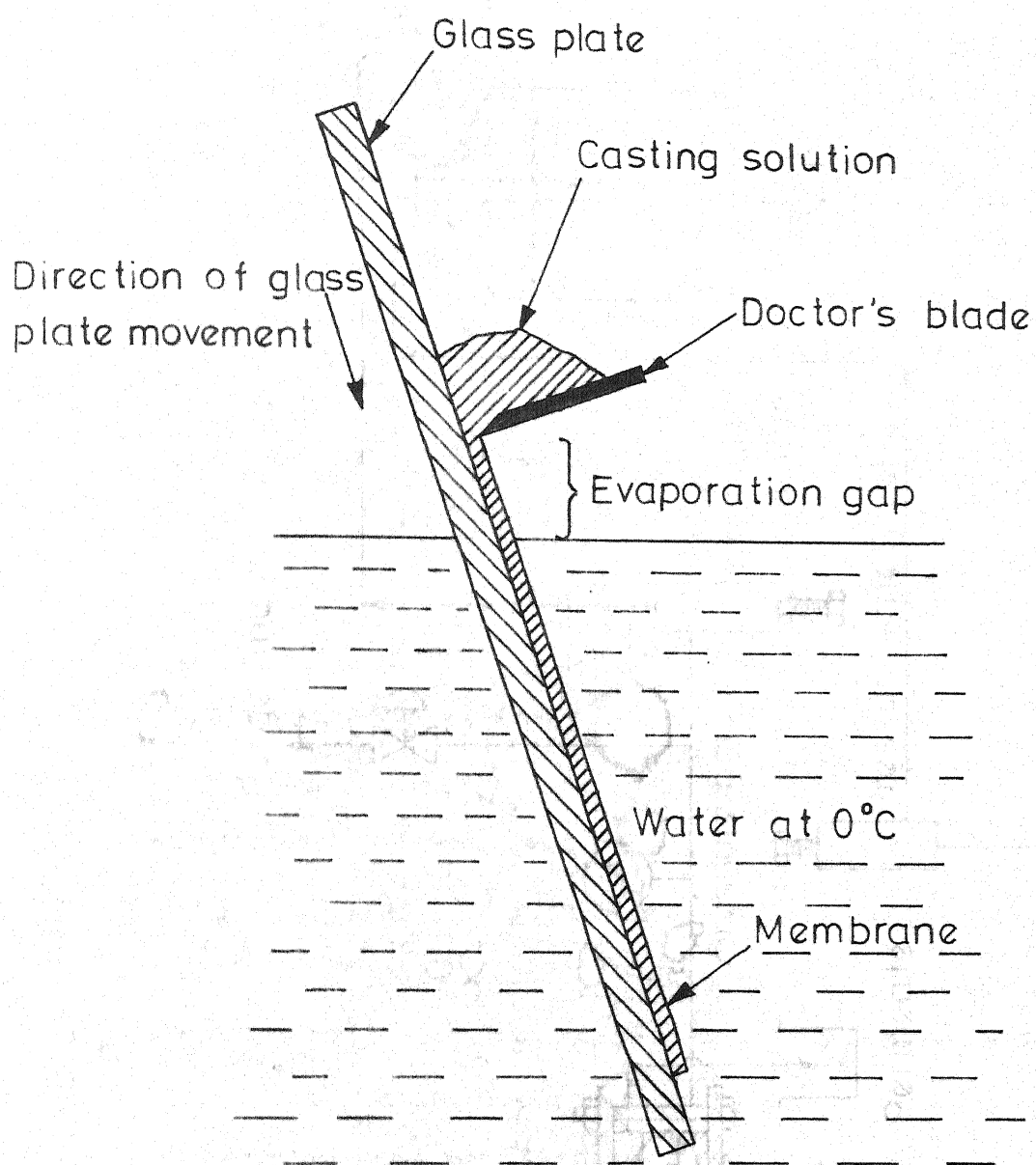


Fig. 3 - Schematic diagram of membrane casting set-up.

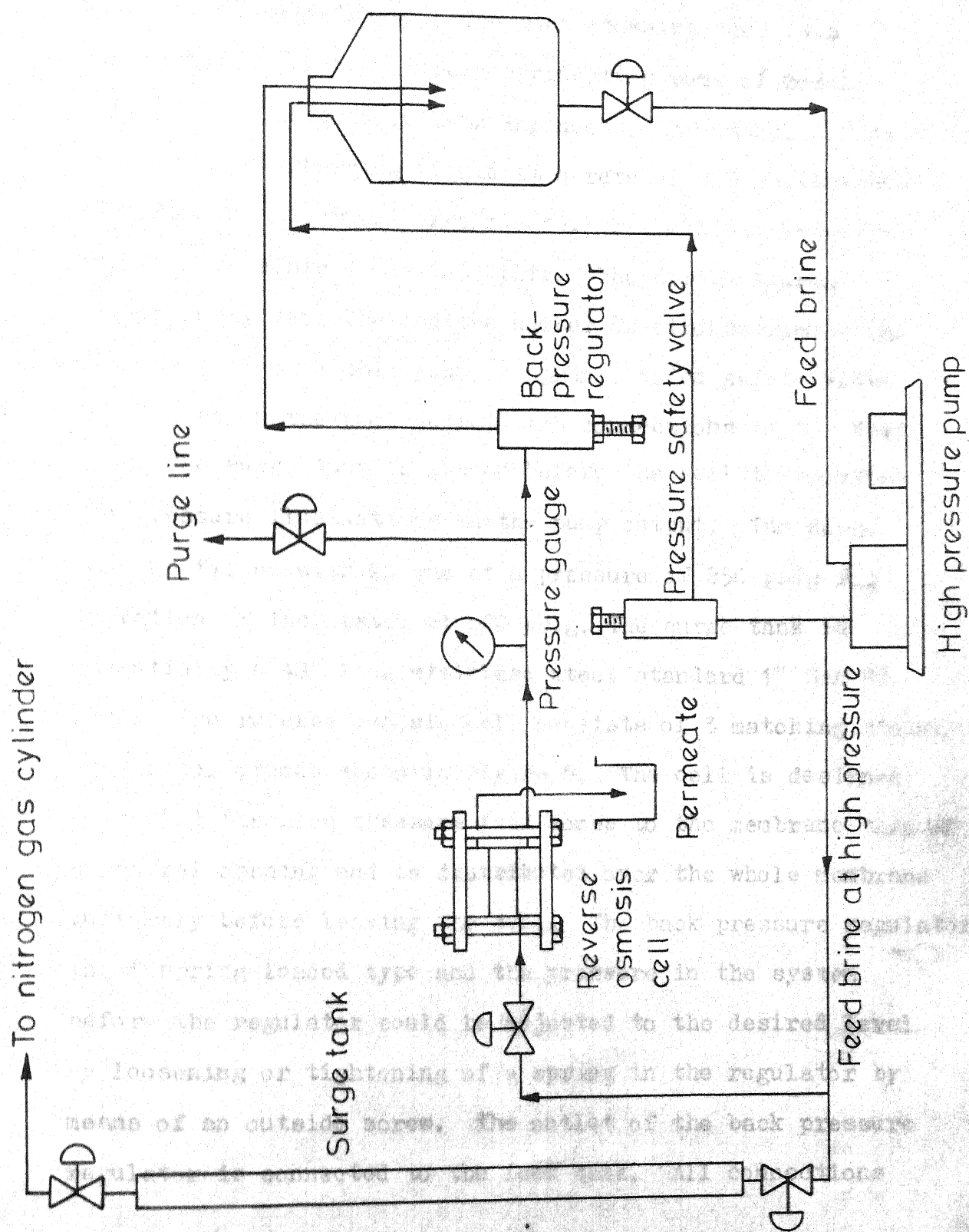


Fig. 4 - High pressure membrane testing loop.

brine are made of stainless steel except the feed tank which is of polyethylene. The high pressure pump is a single acting plunger type reciprocating pump of model UMPN-35 manufactured by Matz Engineers, Ahmedabad. It is capable of discharging liquid at a rate of 8.3 gallons/hour (630 cc/min) at 300 strokes/minute. The maximum pressure that can be achieved is 1350 psig. The stroke length is continuously variable and the number of strokes/minute can also be varied in this pump. A spring loaded safety valve is mounted on the pump outlet with connections to the feed tank. The surge tank is placed before the cell to smoothen out pressure fluctuations in the pump output. The surge tank is filled with  $N_2$  gas at a pressure of 250 psig for operation of the system at 600 psig. The surge tank is essentially a 48" long stainless steel standard 1" Sch 40 pipe. The reverse osmosis cell consists of 3 matching stainless steel pieces shown in Figure 5. The cell is designed such that the high pressure feed comes to the membrane through a central opening and is distributed over the whole membrane uniformly before leaving the cell. The back pressure regulator is of spring loaded type and the pressure in the system before the regulator could be adjusted to the desired level by loosening or tightening of a spring in the regulator by means of an outside screw. The outlet of the back pressure regulator is connected to the feed tank. All connections

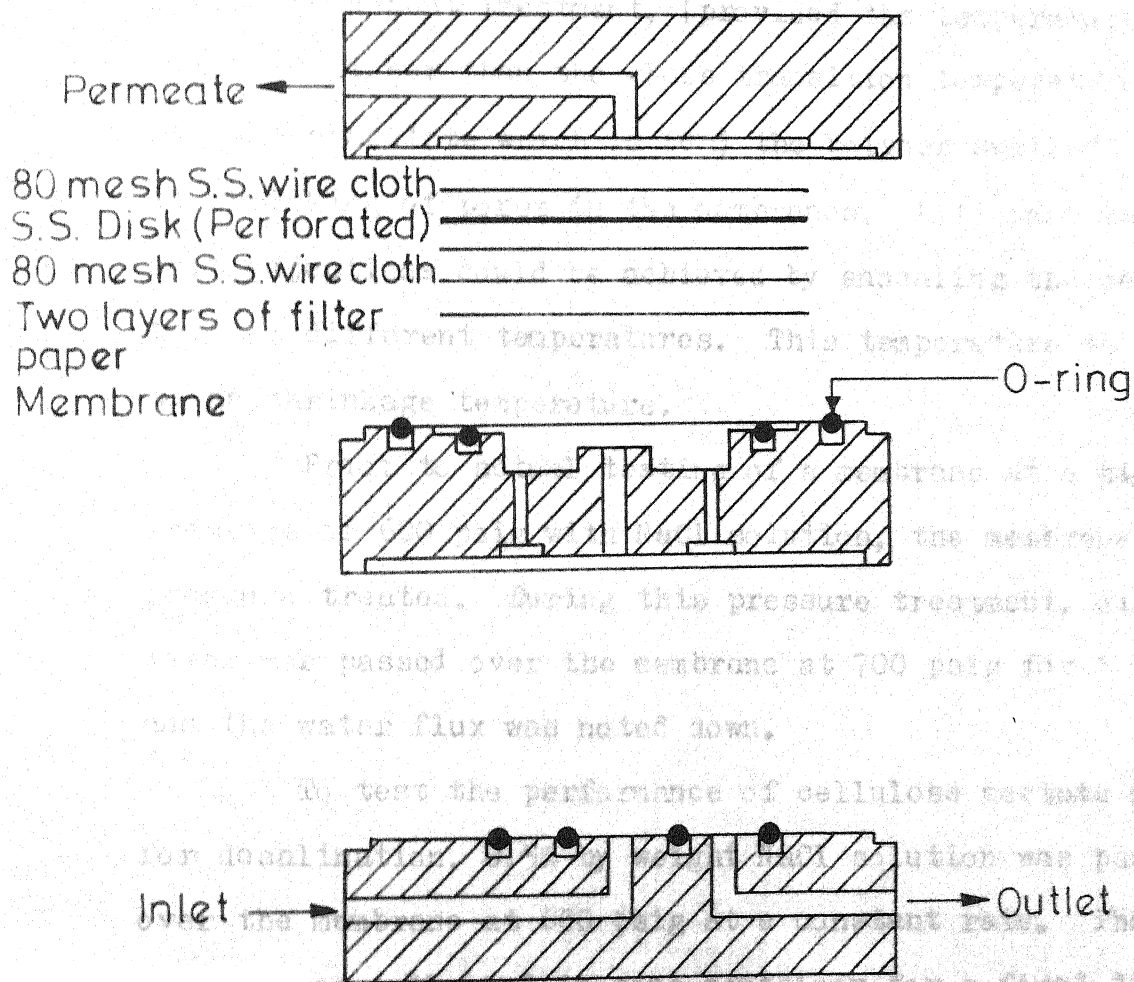


Fig. 5 - Reverse osmosis cell.

between various components were made by means of S.S. Swagelok joints and 1/4" x 1/8" stainless steel tube.

(d) Testing of Membranes at High Pressure:

Cellulose acetate membranes as cast are very porous. For desalination purposes cellulose acetate membrane was immersed in hot water at a specified temperature for 10 minutes followed by immersion in cold water to cool it rapidly. During this heat treatment, (provided the temperature of hot water is higher than the glass transition temperature of cellulose acetate which is 68°C) the polymer swelled resulting in shrinking of pores in the membranes. Different levels of salt rejections could be achieved by annealing the membrane thus at different temperatures. This temperature is referred to as <sup>the</sup> shrinkage temperature.

Prior to actual testing of a membrane at a high pressure of 600 psig with NaCl solution, the membrane was pressure treated. During this pressure treatment, distilled water was passed over the membrane at 700 psig for 1 hour and the water flux was noted down.

To test the performance of cellulose acetate membranes for desalination, 0.5% by weight NaCl solution was passed over the membrane at 600 psig at a constant rate. The permeate was collected in some container for a fixed time after which its volume was measured. Dividing this volume

by the time period of collection and the area of membrane and incorporating proper conversion factors permeate flux can be calculated in gfd. To determine the salt rejection, the salt concentration in the permeate was found out by titrating it against standardized  $\text{AgNO}_3$  solution (concentration 0.05N approximately). This technique is a standard method for estimation of chloride ions in the aqueous solution

## CHAPTER VII

### RESULTS AND DISCUSSION

In the accompanying tables the results of desalination runs with membranes considered largely free of defects are shown. Those results which have been omitted are primarily concerned with exploratory techniques in membrane casting arrangement. Some of the results were manifestly useless because the casting solution had too many microgels which in the membrane under pressure gave rise to salt leakage at their boundary<sup>ies</sup>. These gels also reduced the flux.

The results obtained in this work for evaporation times of less than 0.2 seconds and for cellulose acetate compositions ranging upwards of 27% to 31.5% in Manjikian type casting solution are considered to be the first of its type in desalination membrane literature. It is obvious from experiments 16 to 24 that 30% cellulose acetate compositions give almost as good membranes as the membranes fabricated by Fahey and Grethlein (7), for evaporation times which are less than 0.2 - 0.1 seconds. A look at the solubility diagram of cellulose acetate - acetone - formamide system given in Figure 2 reveals that the 30% CA casting solution used in this work is further away from the solubility curve than the 27.5% CA solution of Fahey and Grethlein. One, therefore, does not have to have a solution very close to the solubility



TABLE 1

PERFORMANCE OF THE MEMBRANES

Cast on Horizontal Table

Sl. No.	Run No.	Composition	Evapora- tion, Time Sec.	Shrinkage Temp., °C	Flux at % Salt 25°C, gfd rejection	Feed Rate ml/min.	Remarks	
1.	24	27.5% CA	5	83	23.2	97.2	460	Casting solution had gels
2.	25	26.0% CA	5	84	22.6	97.1	460	Casting solution had gels
3.	29	26.0% CA	2	83	25.2	96.7	460	Casting solution had gels
4.	35	27.0% CA	<0.5	85	25.0	96.6	460	Solution had lot of gels water was flowing on the membrane
5.	49	26.0% CA	<0.5	87	19.0	97.5	460	Water was flowing on the membrane
6.	50	26.0% CA	<0.5	87	20.9	97.1	460	-do-

TABLE 2

## PERFORMANCE OF THE MEMBRANES

Cast on Vertical Table

Sl. No.	Run No.	Composition	Evapora- time, Time Sec.	Shrinkage Temp., °C	Flux at 25°C, gfd	% Salt rejection	Feed Rate ml/min.	Remarks
7.	76	27.5% CA	<0.2	85	25.2	97.4	520	Solution had gels
8.	80	27.5% CA	<0.2	80	54.2	85.7	520	-do-
9.	81	27.5% CA	<0.2	80	49.3	87.2	520	-do-
10.	94	27.0% CA	<0.1	80	35.4	94.9	600	-
11.	95	27.0% CA	<0.1	85	20.2	97.6	600	-
12.	96	27.0% CA	<0.1	75	60.3	74.7	600	-
13.	101	27.0% CA	<0.1	80	54.0	84.0	600	-
14.	102	27.0% CA	<0.1	85	21.4	97.8	600	-
15.	78	30.0% CA	<0.2	80	26.9	97.7	520	-
16.	84	30.0% CA	<0.2	80	27.5	97.2	520	-
17.	88	30.0% CA	<0.2	85	16.7 17.5	97.9 98.2	520 600	- *
18.	89	30.0% CA	<0.2	85	17.4 17.6	97.8 98.1	520 600	- *
19.	118	30.0% CA	<0.1	75	36.0	96.3	600	

Table 2 (contd.)

Sl. Run No.	Composition	Evapora- tion, Time Sec.	Shrinkage Temp., °C	Flux at 25°C, gfd	%Salt rejection	Feed Rate ml/min.	Remarks
20. 119	30.0% CA	<0.1	78	28.7	96.6	600	* Temperature of casting solution reduced by keeping it in ice-cold water for 15 mts. before casting.
21. 121	30.0% CA	<0.1	80	23.8	96.9	600	
22. 123	30.0% CA	<0.1	70.5	58.5	91.8	600	
23. 124	30.0% CA	<0.1	70.5	69.7	84.8	600	
24. 125	30.0% CA	<0.1	80.0	27.0	97.6	600	
25. 129	31.5% CA	<0.1	70.0	27.5	94.4	600	
26. 130	31.5% CA	<0.1	74.0	23.1	97.1	600	

\*The feed flow rate was increased from 520 ml/min. to 600 ml/min. As in other experiments of this type salt rejection always improved by 0.3 - 0.5% CA due to reduction in concentration polarization - the flux also improves in general by about 1-3 gfd.

26.0% CA refers to 26% CA - 31% Formamide - 43% Acetone  
 27.0% CA refers to 27% CA - 31% Formamide - 42% Acetone  
 27.5% CA refers to 27.5% CA - 31.7% Formamide - 40.8% Acetone  
 30.0% CA refers to 30.0% CA - 25% Formamide - 45% Acetone  
 31.5% CA refers to 31.5% CA - 20.5% Formamide - 48% Acetone

All data reported were taken after the membrane was run for atleast 1/2 hour and represent the values during  $\frac{1}{2}$  to 2 hours from start.

\*\* Membrane Thickness As Cast -

line as claimed by Fahey and Grethlein. However, it may produce a better membrane. Further these membranes give a salt rejection of about 97.6% at annealing temperatures of 80°C and lower. For example, in experiment 26, a 31.5% cellulose acetate membrane has a salt rejection of 97% at an annealing temperature of only 74°C, whereas the membranes of Fahey and Grethlein need annealing at about 82-83°C for a comparable salt rejection. One may envisage membranes from casting solution having cellulose acetate percentage higher than 31.5 which will not need any annealing at all, thus eliminating this step in membrane fabrication altogether. The densification does seem to cause much of a decrease in flux but this aspect needs further investigation.

A further consequence of our results from experiments 7 to 26 is that contrary to McCutchan's results shown in Figure 1, very good membranes can be produced by going to very low evaporation periods if the concentration of cellulose acetate in the Manjikian type casting solution is increased. Since the permeate flux increases with decrease in evaporation time, one encounters interesting possibilities of improving upon existing membranes by controlling the casting solution composition and the evaporation time.

It is useful to compare the results of the present work with those done at Central Salt and Marine Chemicals Research Institute, Bhavnagar-2, Gujarat. The best CSMCRI

results as reported in "A Special Report on Desalination Research at CSMCRI (1964-71)" are:

Feed Mg/lit.	Operating Pressure Psig	% Salt Rejection	Temperature	Product Flux gfd
5200	600	97.4	25°C	15
7000	600	90-95	25°C	16.4

In a recent letter from their Director dated 27th March, 1974 (9) it was stated that, "until 1972 whatever good results were achieved have been included in the special report on desalination research at CSMCRI. However, as far as the new work is concerned, blended composite membrane investigations are in progress for obtaining high flux-high rejection membrane. But we feel that it is only after conducting experiments on higher scale we shall be in a position to make the information available."

When one compares these CSMCRI results with those of the present work as given in Tables one notices that the membranes of this work are 2 - 3.5 times better than the best CSMCRI membranes. Further experiment number 22 in Table 2 indicates an excellent membrane with about 92% salt rejection and 58.5 gfd permeate flux. The best membrane of Fahey and Grethlein (7) in this respect gives only a flux of about 50 gfd with 91% salt rejection. Since the speed of the glass plate entry into the ice-cold bath could not be made absolutely

uniform because it was hand-driven, best membrane performance is not achieved always in our vertical casting apparatus due to possibilities of wavemark formation on the membranes. A mechanical drive would eliminate this complication thus ensuring much higher reproducibility in membrane fabrication.

## CONCLUSION

Highly productive cellulose acetate desalination membranes can be fabricated from Manjikian type casting solutions with cellulose acetate content ranging upwards of 27% to 31.5% if the air exposure period in membrane casting is reduced to around 0.2 seconds. At 600 psig, these membranes are capable of giving a flux of upto 28 gfd with 98% salt rejection from a feed solution containing 0.5% by weight NaCl. Thus membranes having desalination characteristics comparable to or better than those made by Fahey et al. can be obtained from casting compositions having a higher concentration of cellulose acetate at lower evaporation times. Further McCutchan and Johnson's conclusion obtained from membranes with Manjikian composition that very low evaporation period produces membranes with high flux and very poor salt rejection becomes invalid when the casting solution composition is changed.

Membranes produced from casting solutions having 31.5% CA give reasonable flux and salt rejection at an annealing temperature as low as 74°C. This result opens up the possibility of fabricating membranes that do not need any annealing at all.

The best membranes produced in our laboratory are about 2-3 times better than conventional CA membranes used for brackish water desalination and other separations. Extensive savings in capital investment is likely if these types of membranes are used in industrial separations. Further work towards optimizing

the membrane casting solution and casting conditions are in order to improve membrane performance and specifying exact conditions for industrial fabrication of these membranes.

\* \* \*



## REFERENCES

1. Reid, C.E. and Breton, E.J., J. of Applied Polymer Science, 1, 133-143, February (1956).
2. Loeb, S. and Sourirajan, S., University of California, Los Angeles, Department of Chemical Engineering Report No. 60-60, (1960).
3. Manjikian, S., Loeb, S., and McCutchan, J., Proc. First Intern. Symp. on Water Desalination 2, ~~165~~-173 (1967).
4. Lonsdale, H.K. and Podall, H.E., Reverse Osmosis Membrane Research, Plenum Press 1972.
5. Sourirajan, S., Reverse Osmosis, Logos Press 1970.
6. McCutchan, J.W. and Johnson, J.S., Cellulose Acetate Membranes for Desalting Sea Water, at the second Conference on Water Desalination held on 1-3 March 1972 at CSMCRI, Bhavnagar, India.
7. Fahey, P.N. and Grethlein, H.E., Desalination 9, 297-313, (1971).
8. Kesting, R.E., Synthetic Polymeric Membranes, McGraw-Hill Book Company, 1971.
9. Personal Communications of Director of CSMCRI, Bhavnagar with Dr. K.K. Sirkar (Department of Chemical Engineering, IIT-Kanpur).

...

APPENDIXSAMPLE CALCULATIONExperiment No. 118

Vol. of permeate collected = 27.5 ml

Time period of collection = 1/2 hour

Diameter of the membrane exposed to the feed solution  
= 1.25 inches

Average temperature of feed = 31.00 °C

Vol. of permeate =  $\frac{27.5 \times 2 \times 24}{1000}$  litres/day

=  $\frac{27.5 \times 2 \times 24}{1000} \times 0.264$  gallons/day

Permeate Flux =  $\left( \frac{27.5 \times 2 \times 24 \times 0.264}{1000} \right) \left( \frac{4 \times 144}{1.25 \times 1.25} \right)$   
gal/(day)(ft<sup>2</sup>).

= 40.9 gfd

Viscosity of water at 25°C = 0.894 centipoise

Viscosity of water at 31.25°C = 0.7840 centipoise

Permeate Flux at 25°C =  $\frac{40.9 \times 7840}{0.894}$  gfd  
= 36.0 gfd

Salt Rejection:

To prepare standard solution of NaCl in water for standardizing AgNO<sub>3</sub> solution, 0.16 gms of NaCl was dissolved in 250 ml of water.

Concentration of standard NaCl solution =  $\frac{0.16 \times 1000}{250}$  gm/litre  
=  $\frac{0.16 \times 1000}{250} \times \frac{1}{58.44}$  N.

Volume of standard NaCl solution for titration = 5 ml.

Volume of  $\text{AgNO}_3$  solution required = 11.4 ml.

Concentration of  $\text{AgNO}_3$  solution =  $\frac{0.16 \times 1000}{250 \times 58.44} \times \frac{5}{11.4} \text{ N}$

Volume of  $\text{AgNO}_3$  solution required when it is titrated against  
5 ml of permeate = 3.3 ml.

Therefore concentration of NaCl in permeate

$$= \frac{0.16 \times 1000 \times 5}{250 \times 58.44 \times 11.4} \times \frac{3.3}{5} \text{ N.}$$

Concentration of NaCl in permeate in term of mg/litre

$$= \frac{0.16 \times 1000 \times 5 \times 3.3}{250 \times 58.44 \times 11.4 \times 5} \times \frac{58.44 \times 1000}{5}$$

$$= 184 \text{ mg/litre}$$

$$\% \text{ salt rejection} = \left(1 - \frac{184}{5000}\right) \times 100$$

$$= 96.32\%$$

...